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AND OXYGEN CONTAINING ORGANIC COMPOUNDS***

KATARINA BYSTRÖM



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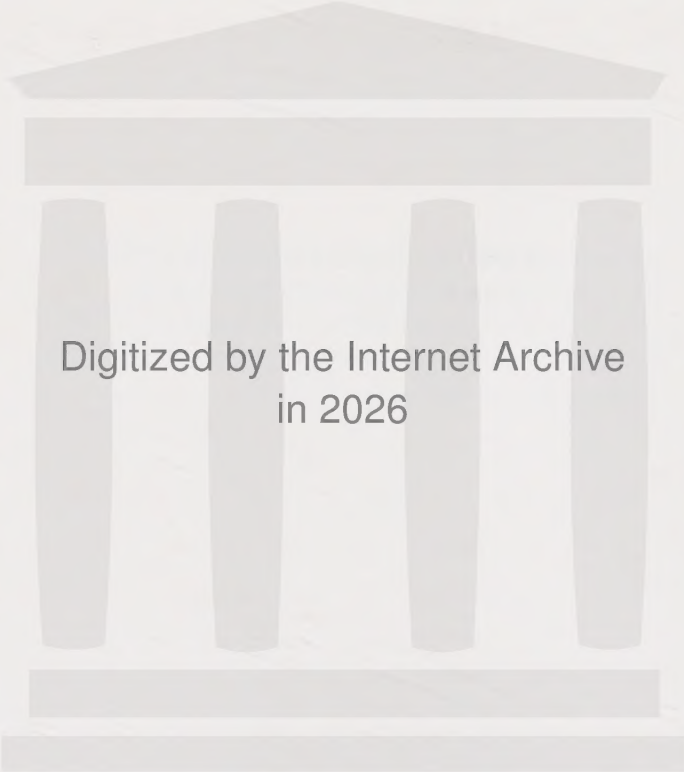
THERMOCHEMICAL STUDIES OF SOME NITROGEN AND
OXYGEN CONTAINING ORGANIC COMPOUNDS

by

Katarina Byström, fil.kand.

Akademisk avhandling som för avläggande av filosofie
doktorsexamen vid matematisk-naturvetenskapliga
fakulteten vid universitetet i Lund kommer att offent-
ligen försvaras å Kemicentrum, Sölvegatan 39, hörsal E,
fredagen den 23 april 1982, kl 10.15.

Lund 1982



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**THERMOCHEMICAL STUDIES OF SOME NITROGEN
AND OXYGEN CONTAINING ORGANIC COMPOUNDS**

KATARINA BYSTRÖM
FIL KAND, MLM

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ANALYTICAL STUDIES OF SOME NITROGEN
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ANALYTICAL STUDIES
OF SOME NITROGEN



1951 1951

Organization LUND UNIVERSITY Thermochemistry Chemical Center P.O.B. 740 S-220 07 LUND, Sweden	Document name DOCTORAL DISSERTATION	
	Date of issue April 1982	
	CODEN: LUNKDL/(NKTK-1003)/1-15 (1982)	
Author(s) Katarina Byström	Sponsoring organization	
Title and subtitle Thermochemical studies of some nitrogen and oxygen containing organic compounds.		
Abstract Determinations of <u>enthalpies of formation</u> of some oxygen and nitrogen containing organic compounds based on <u>combustion</u> and <u>vaporization calorimetric measurements</u> have been reported. The influence on the enthalpy of formation and strain energy from relative positions of the oxygens in various cyclic 1,3- and 1,4-polyethers has been investigated. Calorimetric studies of some cyclic <i>cis</i> and acyclic <i>trans</i> azoxy compounds have been combined with a force-field parametrization for azo N-oxides. Enthalpies of formation and strain energies in the azoxy series are discussed in a comparison with the corresponding values for the azo analogues. A determination of the enthalpy of formation of 1,3,5-triazine and a discussion of stabilization energies in some aromatic nitrogen compounds have been presented. Solid phase transformations in azoxy compounds and some structurally related compounds have been studied by <u>d.s.c.</u> and <u>enthalpies and entropies of transition</u> have been derived.		
Key words		
Classification system and/or index terms (if any)		
Supplementary bibliographical information	Language English	
ISSN and key title	ISBN	
Recipient's notes	Number of pages 15	Price
	Security classification	
Distribution by (name and address)		

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Date 29/3 - 82

This thesis summarizes the work presented in the following papers, which will be referred to by the Roman numerals I-VI.

- I. Enthalpies of Formation of Some Cyclic 1,3- and 1,4-Di- and Polyethers: Thermochemical Strain in the -O-C-O- and -O-C-C-O- Groups.
K. Byström and M. Månsson, J. Chem. Soc. Perkin Trans. 2, in press.
- II. Enthalpies of combustion, vaporization and formation for di-n-propyldiazene N-oxide and di-t-butylldiazene N-oxide.
K. Byström, J. Chem. Thermodynamics 1981, 13, 139.
- III. Enthalpies of formation of cyclic cis azo N-oxides. On the question of vicinal in-plane lone pair - lone pair repulsions.
K. Byström, M. Månsson, U. Ehrbar, D. Crans and J.P. Snyder, in manuscript.
- IV. Molecular Mechanics Studies of Enthalpies of Formation and Strain Energies of Azoxyalkanes.
Katarina Byström, in manuscript.
- V. The Stabilization Energy of 1,3,5-Triazine Derived from Measurements of Combustion and Sublimation.
K. Byström, J. Chem. Thermodynamics, in press.
- VI. Solid-Solid Phase Transitions in Azoxy Compounds.
K. Byström, J. Chem. Soc. Faraday Trans. I, 1980, 76, 1986.

Introduction

The usefulness of accurately determined thermochemical data is demonstrated by their practical and theoretical applications.^{1,2} One of the most useful thermochemical quantities is the enthalpy of formation of a compound from its constituent elements. Knowledge of a large body of accurate enthalpies of formation of carefully selected compounds is a necessity for the establishment of reliable structure-energy relations, which is of a joint interest to theoretical chemists and thermochemists.

The most general method of obtaining enthalpies of formation for organic compounds is from measurements of enthalpies of combustion. The availability of a well-established moving-bomb calorimeter and the applicability of the method to all the compounds studied made combustion calorimetry the obvious choice in this work.

In discussions of intramolecular bond and interaction energies all intermolecular forces must be removed from consideration. Thus, the enthalpy of formation must refer to a hypothetical ideal gas state. The measurement of enthalpies of vaporization and sublimation was therefore an important part of this investigation.

The aim of the work to be discussed here has been to obtain reliable thermochemical quantities, mainly enthalpies of formation, for some oxygen and nitrogen containing organic compounds. For example, the influence on the enthalpy of formation from relative positions of the oxygens in cyclic polyethers has been investigated (paper I). The large difference in thermal stability between azo compounds and their N-oxide counterparts motivated a study of enthalpies of formation of some acyclic *trans*- (paper II) and cyclic *cis*-azoxy compounds (paper III). The results have been used in a force-field parametrization of azo N-oxides (paper IV). The work on azoxyalkanes has been extended to a d.s.c. study of phase transformations and enthalpies and entropies of solid state transitions for some azo N-oxides and structurally related compounds have been reported (paper VI). A study of the stabilization energy of 1,3,5-triazine derived from its enthalpy of formation has been presented in paper V.

Bond energy schemes

The application of bond energy schemes to thermochemical data has two principal aims, the correlation of experimental enthalpies of formation in order to make

predictions for other compounds and the evaluation of stabilizing and destabilizing energy effects. The earliest bond energy schemes made use of constant and transferable bond energy terms, which soon was shown to be an oversimplification. The weakness of such methods is clearly demonstrated by their failure to predict the differing enthalpies of formation for structural isomers. More modern bond energy schemes such as the Group, Allen and Laidler methods introduced parameters accounting for nonbonded interactions between next-nearest neighbours. Schemes of this rather simple type have been successfully applied to a large number of organic compounds (see reference 1, chapter 7). Addition of correction terms for 1,4 and 1,5 steric interactions made it possible to calculate enthalpies of formation also for highly branched compounds. However, numerous compounds have structures for which simple additivity rules are not applicable owing to angle strain, torsional strain, steric crowding and so on.

The availability of large and fast computers has led to the development of more refined bond energy schemes. The force-field method (described in reference 3) is used to find the conformation of the molecule corresponding to minimum energy. The enthalpy of formation is derived as the sum of constant and transferable bond and structural parameters corresponding to certain "natural" bond lengths and angles, and the steric energy consisting of contributions from bond stretching, angle bending, torsional energy and van der Waals and dipole interactions. The force-field method has been successfully applied to various classes of compounds. The calculated enthalpies of formation are usually in fair agreement with experimental results even for strained cyclic systems. A draw-back of molecular mechanics is that since it is an empirical method a large amount of thermochemical and structural information is usually needed before a reliable force-field can be developed.

If one wants to compare energies of compounds which are not structurally similar, e.g. acyclic and cyclic compounds, the enthalpies of formation are not directly informative and discussions are usually made in terms of stabilizing or destabilizing effects relative some reference model compound. The numerical values for apparent strain or stabilization energies will depend directly on the choice of reference system. Thus, strain (or stabilization) energies derived in different ways are seldom directly comparable. It has been customary to relate strain energies of hydrocarbons to the normal alkanes. With this choice of reference system cyclohexane is free of strain. Since normal alkanes larger than propane contain conformations of higher energy at ambient temperatures Allinger refers strain energies to the most stable (all anti) conformations of these compounds.³

Relative this reference system cyclohexane turns out to be strained. This demonstrates the importance of proper identification of the reference model compounds.

Non-bonded interactions in cyclic polyethers

The large influence of structures such as O-C-O and O-C-C-O, respectively, upon the thermochemical stability of straight-chain oxa-compounds has been established.⁴ Relative an aliphatic mono-ether the 1,3-ethers are stabilized, whereas the 1,4-ether is strained. Furthermore, the stabilization energies of 1,3-ethers are directly proportional to the number of next-nearest neighbour oxygen pairs.

The strong energy dependence from relative oxygen positions made it of interest to study some cyclic 1,3- and 1,4-polyethers (paper I). The obtained enthalpies of formation and derived apparent strain energies for the cyclic oxa-compounds of this work are listed in table 1, together with the same quantities for three homologous cyclic 1,3-ethers.^{5,6} The apparent strain energy is defined by the expression:

$$[S] = \Delta H_f^0(g, \text{obs}) - \Delta H_f^0(g, \text{calc}) - mRT \quad (1)$$

where m is the number of rings in the molecule.⁷ The enthalpies of formation of the reference compounds, $\Delta H_f^0(g, \text{calc})$, were derived from an Allen bond energy scheme, using the $\Delta H_f^0(g)$ parameters recommended in reference 1, except for Γ_{OCO} which was taken as $-54.2 \text{ kJ mol}^{-1}$.⁴ Since an Allen bond energy scheme accounts

Table 1. Enthalpies of formation and strain energies of cyclic polyethers.

Compound	$-\Delta H_f^0(g)/\text{kJ mol}^{-1}$	$[S]/\text{kJ mol}^{-1}$
1,3-Dioxane	338.4 ± 1.1	9.5
1,4-Dioxane	316.5 ± 0.9	13.8
1,3,6-Trioxacyclooctane	467.2 ± 1.2	26.6
12-Crown-4-ether	631.1 ± 2.1	32.1
15-Crown-5-ether	799.5 ± 2.0	30.0
S-Trioxane ^a	465.8 ± 0.5	22.3
S-Tetroxane ^a	620.2 ± 0.7	31.3
S-Pentoxane ^b	779.8 ± 1.3	35.3

^a Reference 5.

^b Reference 6.

for interactions between atoms bonded to a common atom, the O-C-O stabilizing effect is part of the reference system, whereas the O-C-C-O destabilization observed in the open-chain oxa-compounds is not.

Relative to straight-chain polyethers all the cyclic ethers exhibit strain. The strain energies of trioxane, tetraoxane and pentoxane $((\text{CH}_2\text{O})_n)$ are directly proportional to the number of 1,3-dioxane units. The "strain increment" is also close to the apparent strain energy of 1,3-dioxane. The derived strain energies of the three ethers with general formula $(\text{CH}_2\text{CH}_2\text{O})_n$ show quite a different pattern, i.e. there does not seem to be any constant contribution to the strain energy per 1,4-dioxane unit. In fact, the highest destabilization is found for the 12-crown-4-ether. However, one would expect additive stabilization and destabilization effects only for structural units that are similar in terms of bond lengths, bond angles, dihedral angles and steric interactions. Thus, the constant strain energy per O-C-O unit seems reasonable, since the preferred arrangements of the O-C-O structures in 1,3-dioxane, trioxane and tetraoxane are similar with all carbon-oxygen bonds gauche. A comparison of the molecular structures of 1,4-dioxane, 12-crown-4-ether and 15-crown-5-ether shows that there are large differences in the conformations of the dioxane units that constitute these rings. While 1,4-dioxane consists of two ggg units, the crown ethers adopt unusual conformations containing gga, aga and aaa units.⁸ Since the different arrangements of the O-C-C-O unit have different energies, there is no constant strain energy increment per next-next-nearest-neighbour oxygen pair. It was shown in paper I that by choosing a reference system consisting of hypothetical isomers not only with the same sequence of atoms but also with the same conformations of the different 1,4-dioxane units, the strain energies of 1,4-dioxane, 12-crown-4-ether and 15-crown-5-ether are reduced to 4.2, 8.7 and 11.2 kJ mol⁻¹, respectively. This corresponds to a destabilization of 2.1-2.2 kJ mol⁻¹ per oxygen-oxygen interaction. Thus, relative a reference system that accounts for conformational differences the strain energy increment is constant.

A direct comparison of strain energies of cyclic ethers and cycloalkanes is in most cases not meaningful, since the medium-sized polyether rings generally adopt conformations not encountered in the cycloalkanes. Since most cycloalkanes have strong H...H repulsions across the rings, the major contribution to the differential strain ($[S]_{\text{ether}} - [S]_{\text{alkane}}$) is not non-bonded oxygen interactions but rather steric repulsions in the cycloalkane. However, the six-membered rings are an exception. Cyclohexane, tetrahydropyran, 1,3-dioxane, 1,4-dioxane and 1,3,5-trioxane exist exclusively in a chair form. The change in enthalpy of formation when a methylene group in cyclohexane is replaced by an ether oxygen is -100.0

kJ mol^{-1} , which is 4.8 kJ mol^{-1} less negative than the open-chain increment.¹ The apparent strain of the cyclic ethers relative their acyclic counterparts can partly be attributed to the difference in ether increment. Relative the cyclic mono-ether 1,3-dioxane and trioxane are stabilized. The average stabilizing effect is 14.3 kJ mol^{-1} per next-nearest-neighbour oxygen pair, which can be compared with the open-chain value of 17.6 kJ mol^{-1} . Thus, the apparent strain in cyclic 1,3-ethers can be divided into two major contributions, the different ether increment and the reduced O-C-O stabilizing effect. Compared to tetrahydropyran 1,4-dioxane is strained by 6.9 kJ mol^{-1} . Thus, in addition to the 4.8 kJ mol^{-1} arising from the reduced ether increment, the apparent strain per oxygen of having a pair of oxygens in 1,4-position is approximately 3.5 kJ mol^{-1} .

In view of the results for cyclic 1,4-ethers the derived destabilization of 1,2-diethoxyethane (9.9 kJ mol^{-1})⁴ seems quite large. But the apparent strain is probably in part a result of the presence of conformers with higher energy. Investigation of the gas-phase molecular structure of dimethoxyethane showed that it contains an equilibrium mixture of several conformers.⁹ Using the results by Podo *et al.*¹⁰ one can estimate the energy of the equilibrium mixture as 4.5 kJ mol^{-1} above the most stable conformer (all anti). In reference 11 "strainless" enthalpy parameters for ethers are given, derived in such a way as to fit experimental $\Delta H_f^0(\text{g})$ values corrected for conformational and torsional contributions. The derived "strainless" enthalpy of formation for diethoxyethane becomes $-421.8 \text{ kJ mol}^{-1}$. The difference of 13.6 kJ mol^{-1} between the observed and "strainless" enthalpy of formation can be divided into torsional and conformational contributions and a possible O-C-C-O destabilization. Taking the torsional energy as 6.3 kJ mol^{-1} ¹¹ and assuming the conformational energy to be the same as in dimethoxyethane, the strain that can be attributed to the 1,4-dioxane unit is reduced to 2.8 kJ mol^{-1} .

Enthalpies of formation and strain energies of azoxy compounds

Small fragments such as CO, SO, SO_2 , N_2 and N_2O incorporated in a carbon skeleton can be extruded producing the corresponding hydrocarbon. Heteroextrusion reactions for azo compounds and the corresponding N-oxides have received considerable attention during recent years.¹²⁻¹⁴ The fragmentation of both the cyclic azo and azoxy systems occurs via a concerted pathway, but the relative rate for N_2 vs. N_2O loss is in the order of 10^{17} at 298.15 K. The corresponding difference in energy barriers is 96 kJ mol^{-1} , which is remarkably large for two processes differing formally only in the N-oxide perturbation. In order to get a better understanding of the

origin of the difference in reactivity of azo- and azoxyalkanes knowledge of their thermochemical properties was needed. The relative stability of *trans* and *cis* isomers and the magnitude of ring strain in *cis*-azoalkanes and their N-oxide counterparts were two questions of immediate interest. Engel *et al.* have determined enthalpies of formation for a number of diazenes.^{15,16} Enthalpies of formation for two acyclic *trans*- and five cyclic *cis*-azoxy compounds are reported in papers II and III, respectively. However, among the available experimental results only few refer to directly comparable structures. The experimental study was therefore combined with a development of a force-field for azo N-oxides (paper IV), which together with an azo compound force-field¹⁷ permits an extension of comparisons to compounds for which experimental information is lacking.

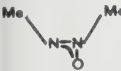
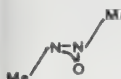
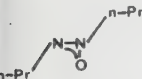
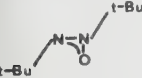
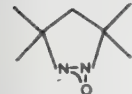
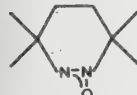
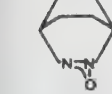
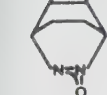
The observed enthalpies of formation for azo N-oxides together with those calculated by molecular mechanics are given in table 2. The average deviation between experimental and calculated values is 1.7 kJ mol^{-1} .

A comparison of experimental (or calculated) enthalpies of formation for azo and azoxy compounds shows that the oxidation of the azo to the azoxy moiety is highly exothermic, whereas the oxidation of N_2 to N_2O is endothermic. The introduction of the N-O bond lowers the enthalpy of formation by 63 to 84 kJ mol^{-1} , a result of the formation of a new σ -bond, but also of the π -electron delocalization over the three heteroatoms.

In figure 1 the energy profiles for the heteroextrusion reactions for 2,3-diazabicyclo[2.2.2]octa-2,5-diene and the analogous N-oxide are shown. Semiempirical potential energy surface calculations for the N_2 and N_2O fragmentations indicated that both ground state and transition state effects attenuated $E_a(\text{azoxy})$ relative to $E_a(\text{azo})$.¹⁴ This is supported by the representation in the figure, but the ground state energy difference seems to be the dominant contribution.

It has been argued that the *cis*-azo group is of higher energy than the *trans* as a consequence of nitrogen lone pair repulsion.¹⁸ If lone pair - lone pair repulsion is the determinant in destabilizing *cis*-azoalkanes, the replacement of one of the lone pairs with a nitrogen-oxygen bond ought to show some significant changes of the strain energies in the azo N-oxide series relative to the corresponding diazenes. In papers III and IV apparent strain energies for *cis*-azo- and azoxyalkanes were derived in two different ways. The results are listed in table 3. $[S]_I$ was derived relative to an All bond energy scheme as given by equation 1, whereas $[S]_{II}$ was defined as the difference between the calculated and the strainless enthalpy of formation both derived from force-field parameters. Since only calculated quantities are utilized in the derivation of $[S]_{II}$ the comparison of strain in azo compounds relative to their azoxy

Table 2. Observed and calculated enthalpies of formation of azoxy compounds.

Compound	$\Delta H_f^0(g)/\text{kJ mol}^{-1}$		$\Delta(\Delta H_f^0(g))/\text{kJ mol}^{-1}$
	obs	calc	
		85.8	
		60.7	
	-31.0 ± 1.4	-30.1	-0.9
	-107.6 ± 2.1	-108.1	0.5
		-22.4	
	-26.5 ± 2.3	-26.6	0.1
	127.8 ± 1.4	128.3	0.5
	92.4 ± 1.8	89.5	2.9
	221.0 ± 2.1	225.7	-4.7
	226.1 ± 1.9	223.8	2.3

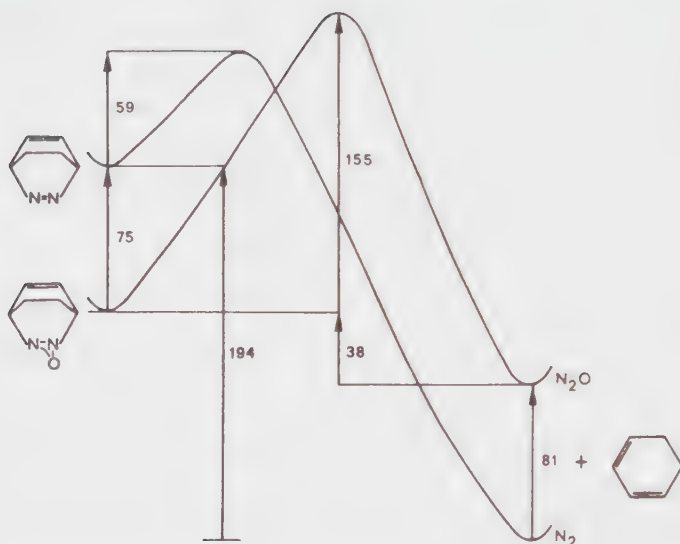


Figure 1. The energetics for an azo and azoxy heteroextrusion reaction (in kJ mol⁻¹).

counterparts could be extended to pairs for which experimental results were not available. Since $[S]_I$ and $[S]_{II}$ were derived using different bond energy schemes based on different reference systems (see paper IV) the two quantities are not directly comparable.

It should be pointed out that the enthalpy parameters utilized in the derivation of strain energies for the *cis* compounds were calculated from *trans* compounds. Consequently, the strain energies contain an implicit contribution from the *trans* to *cis* isomerization energy. The results that the *cis*-diazenes exhibit less strain than their N-oxide analogues can well arise from this source. PRDDO+ calculations on *cis*

†Partial retention of diatomic differential overlap.

Table 3. Strain energies of cyclic *cis*-azo and azoxy compounds (in kJ mol⁻¹)

Compound	Azo		Azoxy	
	[S] _I	[S] _{II}	[S] _I	[S] _{II}
	8.4	12.9		26.5
	31.6	26.6	44.9	46.3
	59.3	58.1	61.5	61.0
	36.1 ^a	43.3	46.6	45.6
		55.9	61.6	63.4
		167.8	171.9	169.1

^a Estimated from corresponding diazene with methyl groups at the bridge-head carbons.

trans pairs indicate that the isomerization energy is 12 to 17 kJ mol⁻¹ higher for the N-oxides than for the azo compounds (paper III) whereas there is no significant difference in the isomerization energy calculated by molecular mechanics for the azo- and azoxy-methanes (paper IV and reference 17).

The variation of strain vs. structure for the two classes of compounds is similar and one may conclude that structurally similar diazenes and diazene N-oxides exhibit nearly identical internal strain. In contrast to alkanes and alkenes, the five-membered azo- and azoxyalkanes are less strained than their six-membered counterparts. Analysis of the steric energies derived in paper IV indicates that the strain energy difference between the five- and six-membered rings can be entirely related to increased angle strain in the latter. The bicyclic azo and azoxy compounds are less strained by 20 to 40 kJ mol⁻¹ relative the corresponding alkenes.¹⁹ The smaller natural C-N-N bond angle in diazenes and diazene N-oxides compared to the C-C=C angle in alkenes is presumably the reason why the azo and azoxy groups are more easily incorporated in strained ring systems.

The energetic similarities between *cis*-azo and azoxy compounds permitted an analysis of the importance of lone pair repulsions in destabilizing the *cis*-azo group relative its *trans* counterpart. The replacement of one of the lone pairs by an N-O bond seemed to have little impact on the overall destabilizing effects of the systems. These results are supported by a calculation of electron repulsion integrals of localized molecular orbitals of PRDDO optimized geometries for the *cis* and *trans* isomers of azo- and azoxymethane. It was found that lone pair-lone pair, bond-lone pair and bond-bond repulsions were of the same order of magnitude. The most important result of this analysis was that for both compounds the major contribution to the energy differences between the *cis* and *trans* isomers was C-H...H-C interactions between the methyl groups. This is in agreement with the expanded CNN angle in acyclic *cis*-azoalkanes (and azoxyalkanes) in comparison with *trans* isomers, in spite of the resulting increase in lone pair-lone pair (or bond-lone pair) repulsions. Thus, consideration of structural determinations (X-ray, PRDDO geometry optimization), apparent strain energies and electron repulsion integrals converge towards the interpretation that *cis*-azo and azoxy compounds are destabilized by steric effects in the hydrocarbon part of the molecules and not by unfavourable interactions in the hetero unit.

Stabilization in nitrogen aromatic compounds

The general stabilization of benzenoid compounds as a result of π -electron delocalization is well known. One way of deriving stabilization energies of aromatic compounds from thermochemical data is to compare observed enthalpies of formation with estimated values for the corresponding Kekulé structures. The difference is defined as the conventional stabilization energy. It should be pointed out that the stabilization energy derived from thermochemical results is a measure of overall stabilizing and destabilizing effects and, thus, has contributions other than the π -electron

delocalization energy. Some important factors are the change in hybridization relative the reference compound and ring strain energy.

When estimating stabilization energies for aromatic compounds there is a basic problem in deciding what bond energy terms to use in the derivation of the enthalpies of formation for the Kekulé structures. One needs a value for the central bond in an $=x-y=$ structure, but any open-chain model compound containing this unit is itself conjugated and thereby stabilized. For aromatic nitrogen compounds there is an additional problem, since experimental data for compounds containing a carbon - nitrogen double bond are limited, and the estimation of the value for $E(C=N)$ is therefore somewhat uncertain.

In reference 20 an estimation of stabilization energies of benzene, pyridine and the three isomeric diazines was made, which gave two rather surprising results. Firstly, a large regular decrease in stabilization was found for substitution of $-CH=$ by $-N=$. An extrapolation of the results would in fact give a destabilization for 1,3,5-triazine. Secondly, pyridazine, which has two energetically different valence bond structures, turned out to be more stable than the 1,3- and 1,4-diazines. The enthalpies of formation for the Kekulé structures were based on bond energies from Cottrell.²¹ It was argued that some of the bond energies used, especially those involving nitrogen, were likely to be in error.

In paper V, where the experimental results for 1,3,5-triazine were reported, it was shown that the use of more up to date bond energy terms changed the picture completely. The results are given in table 4. The enthalpies of formation for the

Table 4. Conventional stabilization energies.

Compound		Stabilization energy / kJ mol^{-1}
Benzene	(22)	191.7
Pyridine	(23)	176
Pyridazine	(20)	137 ^a
Pyrimidine	(20)	170
Pyrazine	(20)	171
s-Triazine	(V)	188

^a Relative the Kekulé structure with an N-N single bond.

Kekulé structures were derived from a Laidler bond energy scheme.¹ (For choice of parameters see paper V.) In this comparison a more reasonable result was obtained. The stabilization energy of pyridazine turns out to be significantly lower than those of the two other diazines. Furthermore, the successive replacement of $-\text{CH}=$ by $-\text{N}=$ does not give rise to a decrease in stabilization. In fact, s-triazine shows the highest stabilization of all the nitrogen containing compounds, but the difference in stabilization between pyridine, pyrimidine, pyrazine and triazine is quite small bearing in mind the uncertainty associated with the bond energy value for the $\text{C}=\text{N}$ bond.

Phase transitions in azoxy compounds

A complete understanding of phase transformations in molecular crystals requires investigation of its various aspects by several methods. Studies of crystal structures, dielectric constants, n.m.r. spectra and thermal properties are usually needed in order to explain the most important aspects of such phase changes. Thermochemical data are particularly useful in interpreting solid-solid transitions where order-disorder effects are predominant.²⁴ Studies of thermal properties are usually performed by adiabatic calorimetry. Valuable information such as transition enthalpies and entropies can also be obtained by differential scanning calorimetry (d.s.c.).

In connection with the combustion calorimetric study of azoxy compounds it was found that most of the substances investigated exhibited highly energetic solid-solid transformations (paper VI). A large solid state transition is an indication of a disordered high-temperature phase, which is often reflected in a low entropy of fusion. Compounds with fusion entropies below the arbitrary limit of $20 \text{ J K}^{-1} \text{ mol}^{-1}$ set by Timmermanns are referred to as plastic crystals. For instance, diazabicyclooctene N-oxide and diazatricyclononene N-oxide have large solid-solid transitions, whereas their fusion entropies are well below $20 \text{ J K}^{-1} \text{ mol}^{-1}$. This means that these compounds form plastic crystals in their high-temperature phases. The solid phase transition entropies for the N-oxides are 6.3 and $14.5 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively, larger than corresponding quantity for bicyclooctane.²⁵ These results were rationalized in a simple symmetry model. Compared to bicyclooctane the two N-oxides have respectively one and two "odd" sides, which can be distributed in three and six ways, respectively. This corresponds to additional entropy increments of $R \ln 3 = 9.1$ and $R \ln 6 = 14.9 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively, in fair agreement with experimental results. Such a simple model works well for bicyclooctene-bicyclooctane ($\Delta(\Delta S_{\text{trs}}) \approx R \ln 3$)²⁵ whereas norbornadiene and norbornane, which have the same symmetry, have quite different entropies of transition ($\Delta(\Delta S_{\text{trs}}) = 12.7 \text{ J K}^{-1} \text{ mol}^{-1}$).²⁵ The results for two other bicyclic N-oxides are given

Table 5. Entropies of transition for two azoxy compounds and corresponding hydrocarbons.

	Transition	T / K	$\Delta S / \text{J K}^{-1} \text{mol}^{-1}$
	T_1	312	36.2 ± 0.9
	fusion	330	4.5 ± 0.2
	T_1	303	26.8 ± 0.3
	fusion	370	5.5 ± 0.2
	T_1	164	27.9^a
	T_1	131	31.4^a
	T_2	306	0.3^a

^a Reference 25

in table 5, together with the transition entropies for the corresponding symmetric hydrocarbons. The entropy differences between N-oxide and hydrocarbon are 8.3 and $-4.9 \text{ J K}^{-1} \text{mol}^{-1}$, respectively, which can be compared with $14.9 (R \ln 6)$ and $5.8 (R \ln 2)$ $\text{J K}^{-1} \text{mol}^{-1}$ expected from symmetry considerations, thus demonstrating that a simple symmetry model in many cases is an oversimplification. It should be pointed out that the d.s.c. measurements were limited to temperatures above approximately 200 K and hence possible transitions below that temperature could not be detected under these conditions.

Di-*t*-butyldiazene N-oxide and the corresponding azo and alkene analogues all have large solid state transitions, and therefore disordered high-temperature phases, but the entropies of fusion for these compounds are still quite large ($\sim 40 \text{ J K}^{-1} \text{mol}^{-1}$). The sum of transition and fusion entropies for the N-oxide, diazene and hydrocarbon are 71.0 , 59.9 and 61.1 kJ mol^{-1} , respectively. The large overall entropy increments seem reason-

able considering the large number of conformations obtainable by rotation of the t-butyl and methyl groups. The additional entropy of $10 \text{ J K}^{-1} \text{ mol}^{-1} \approx R \ln 3$ for the N-oxide could possibly be ascribed to three staggered conformations of the oxygen the t-butyl group bonded to the same nitrogen.

Acknowledgements

I am very grateful to all friends and colleagues at the Thermochemistry Laboratory and other departments at the Chemical Center, who have helped in many different ways. Especially to Margret Månsson, who introduced me into combustion calorimetry, for support, encouragement and many helpful suggestions throughout this work. I wish to express my thanks to Gunilla Gräntz, who performed the vaporization measurements, for her friendship and cooperation. I am also grateful to Gerd Hornemark and Nancy Simsen for their skilful typing of the manuscripts. I would have liked to thank Stig Sunner for his encouragement and many inspiring discussions.

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